DEVELOPMENT OF BULK NANOCRYSTALLINE CEMENTED TUNGSTEN CARBIDE FOR INDUSTRIAL APPLICATIONS

THE UNIVERSITY OF UTAH

Project Partners

University of Utah

Idaho National Engineering and Environmental Laboratory

Kennametal, Inc.

Smith Bits / Smith International, Inc.

Goals

- Develop energy efficient powder synthesis and sintering processes
- Develop *bulk* nanocrystalline WC-Co composite with <100 nm grain sizes

Challenges

- How to produce *bulk* nancrystalline WC-Co? Or any other *bulk* nanocrystalline materials?
- How to produce them in an energy efficient manner and economically?

Benefits

Economic benefits will be realized through increased durability and reliability of wear-resistant materials and tools, resulting in improved productivity.

Energy benefits will be achieved through the use of a more energy-efficient process for the manufacture of tungsten carbide powders and a reduction in the sintering cycle time used for component fabrication.

Barriers

- Lack of knowledge about the feasibility of producing nanosized WC-Co powders with sufficient uniformity in size, composition, and yield,
- Lack of control in maintaining the grain size of materials below 100 nm during sintering at high temperature; and
- Lack of information on the mechanical properties of bulk structures with nanoscale grain size.

Pathways

- Producing uniformly mixed nanosized WC as well as directly producing cobalt-coated WC powder by the vapor phase co-reduction of chloride vapor mixtures with controlled grain sizes and cobalt content.
- Develop a ultrahigh pressure rapid heating and HIPing (UPRH) and ultimately economically viable semi-continuous process for the consolidation of nanostructured WC-Co powder.

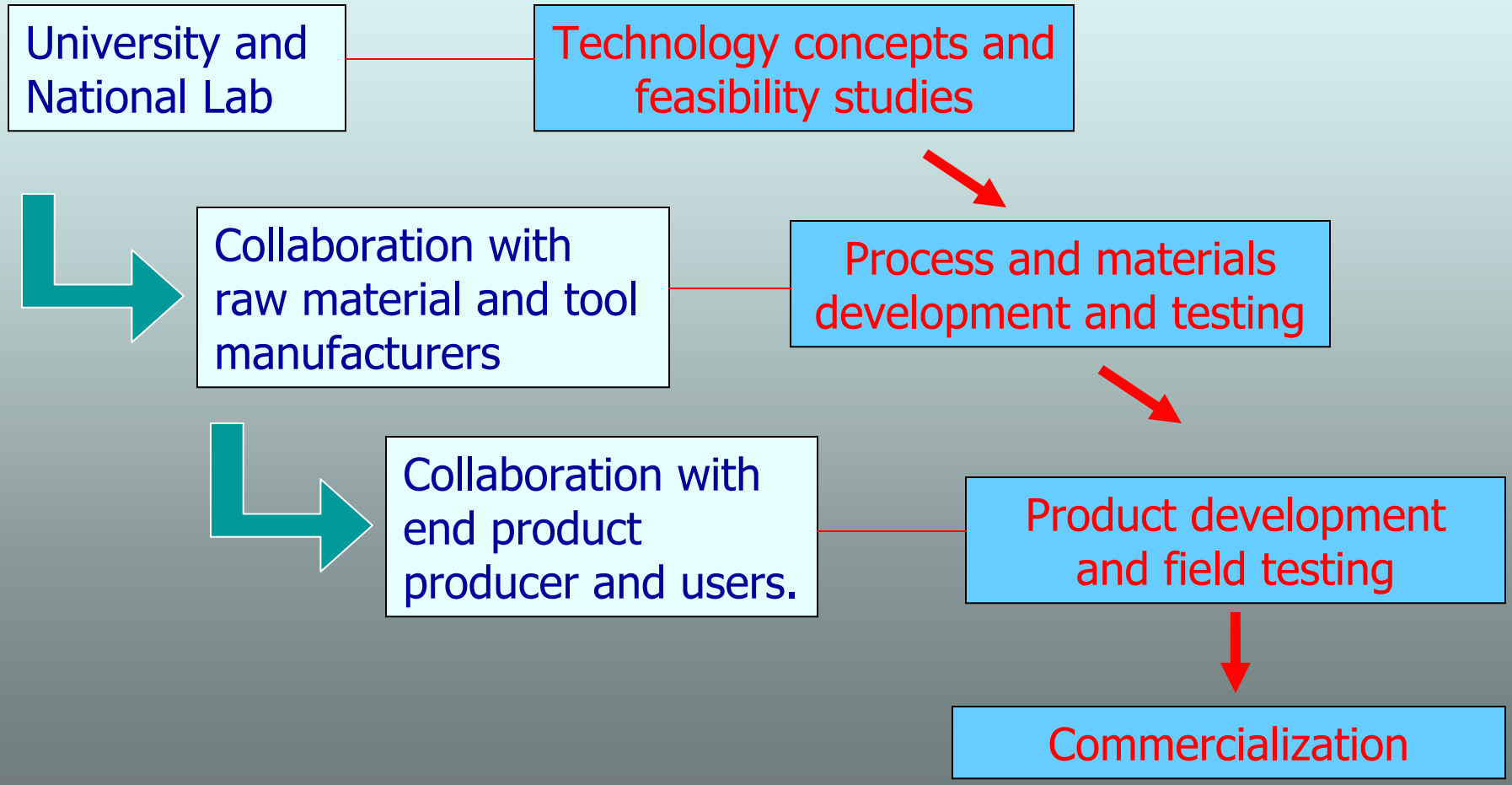
Pathways

- Sintering nano powders while achieving less than 100 nm grain size in the consolidated bulk WC-Co cermets;
- Understanding strengthening and toughening mechanisms through microstructural evaluation and mechanical property testing;
- Optimizing the microstructure of and developing superior mechanical properties for the bulk nanocrystalline materials,
- Evaluation test components in various applications.

Critical Metrics

- Particle / grain size of nanocrystalline WC/Co must be below 50 nm, with chemical compositions within commercial tolerable range,
- Consolidated bulk WC-Co composite must have grain size below 100 nm,
- The powder synthesis and consolidation processes must be at least 20% more energy efficient than the corresponding conventional processes.

Commercialization Path

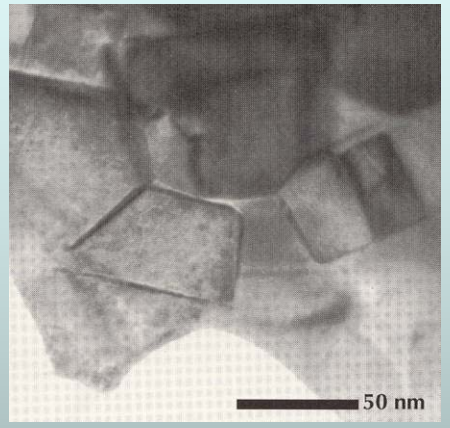


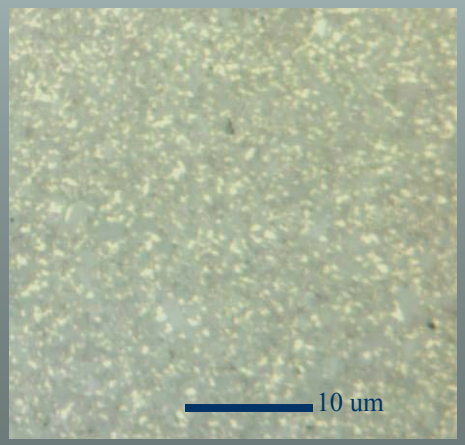
Cemented Tungsten Carbide

- Cemented tungsten carbide, also known as cermets or hardmetals, is a class of very important industrial materials used in metal cutting, oil exploration, mining, and many manufacturing sectors of the economy
- Global market for cemented tungsten carbide tools and parts is estimated to be around US$8 billion annually
- Moderate improvements in its performance could result in huge savings and productivity gains
- Performance limited by relatively low toughness, catastrophic failures
- nanostructured WC-Co offers an opportunity to dramatically improve properties

Nanostructured cemented tungsten carbide -

- Nanostructured WC/Co powder was first developed over a decade ago
- Commercialization is stalled because grain sizes after sintering is no longer nanoscale, thus mechanical properties are similar to conventional WC-Co. Harder, not tougher
- No consolidation technology is available, yet, that can produce bulk WC-Co with <100 nm grain structure while achieving 100% density
- Mechanical properties of "nanostructured" WC-Co remain unexplored.





Chemical Vapor Synthesis of Nanocrystalline Powders

Primary Concept

- Produce mixtures of nanosized powders from precursors
- Reducing a vapor-phase mixture of chlorides of constituent metals
- Reducing agent: H_2, CH_4, C_2H_2, Mg(g)

Powders Successfully Made by CVS

Nickel Aluminide (Ni_3Al)

$3NiCl_2(g) + AlCl_3(g) + 4.5Mg(g) = Ni_3Al(s) + 4.5MgCl_2(g)$

Titanium Aluminide (TiAl)

$TiCl_3(g) + AlCl_3(g) + 3Mg(g) = TiAl(s) + 3MgCl_2(g)$

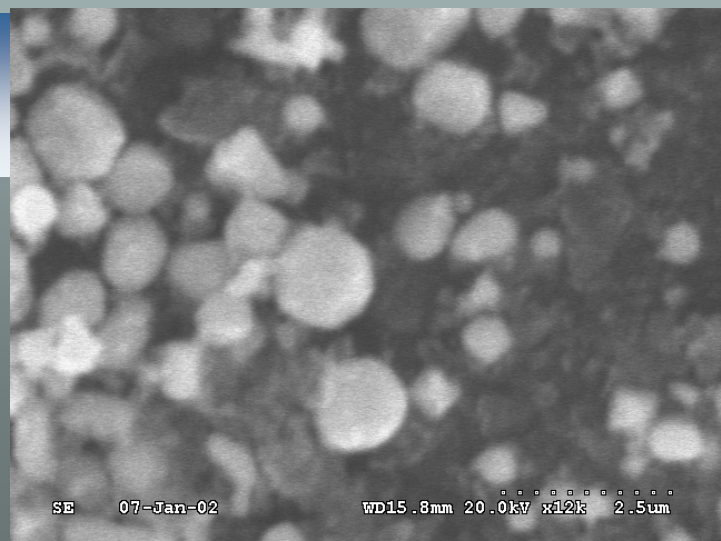
Ni_4Mo

$TiCl_3(g) + AlCl_3(g) + 3Mg(g) = TiAl(s) + 3MgCl_2(g)$

FeCo

$FeCl_2(g) + CoCl_2(g) + 2H_2(g) = FeCo(s) + 4HCl(g)$

FeCo powder



Advantages of the CVS process:

- Homogeneity at atomic level,
- Flexibility in alloying or doping the powder,
- Possibility to produce <30 nm powders.

Disadvantages:

Many hurdles ahead!

Conventional Method

Tungsten ore

Alkali dissociation
Impurity removal

Concentration
Crystallization

} Aqueous Process

Ammonium paratungstate

Calcination

Reduction of WO_3, $WO_{2.9}$

} High-temperature Process

Tungsten powder

Carburization

} High-temperature Process

Tungsten Carbide Powder

Energy-intensive
&
Environmentally unfriendly Process

New processes for making nanocrystalline WC since 1980's

- Spray conversion process to make WC/Co compsoite powder - Rutgers / Nanodyne
- Direct gas phase reaction to produce WC from ammonium metatungstate,
- Co-precipitation of cobalt with salts of tungsten,
- Mechanical milling plus gas phase reduction and carburization,
- High energy milling,
- DC arc plasma
- Integrated mechanical and thermal activation using Co and tungsten oxide and graphite,
- Chemical vapor synthesis of monolithic WC

Synthesis of WC-Co Composite Powder

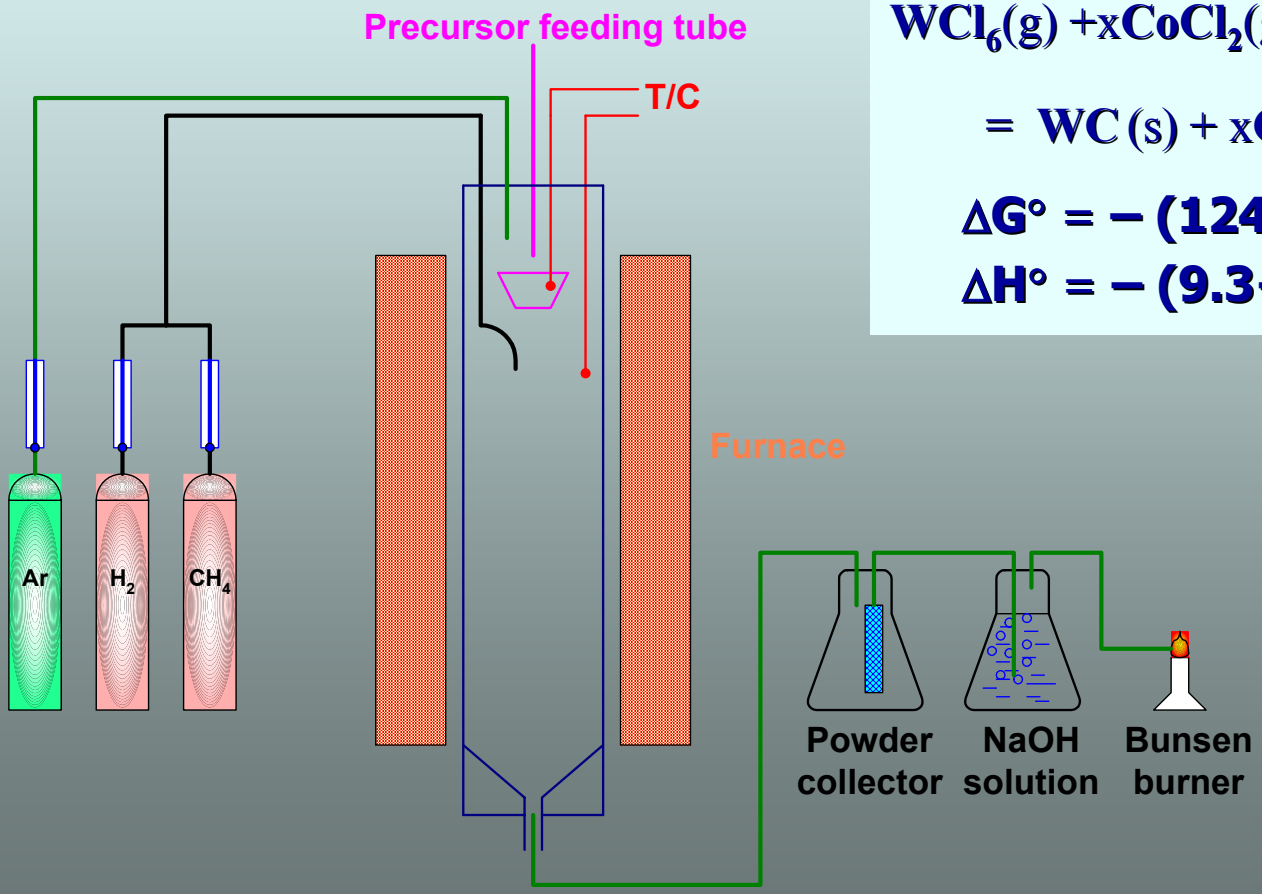
Thermodynamics of synthesis reaction

$$WCl_6(g) + xCoCl_2(g) + CH_4(g) + (x+1)H_2(g)$$

$$= WC(s) + xCo(s) + (2x+6)HCl(g)$$

$\Delta G° = -(124+14x)$ kcal at 1200 K

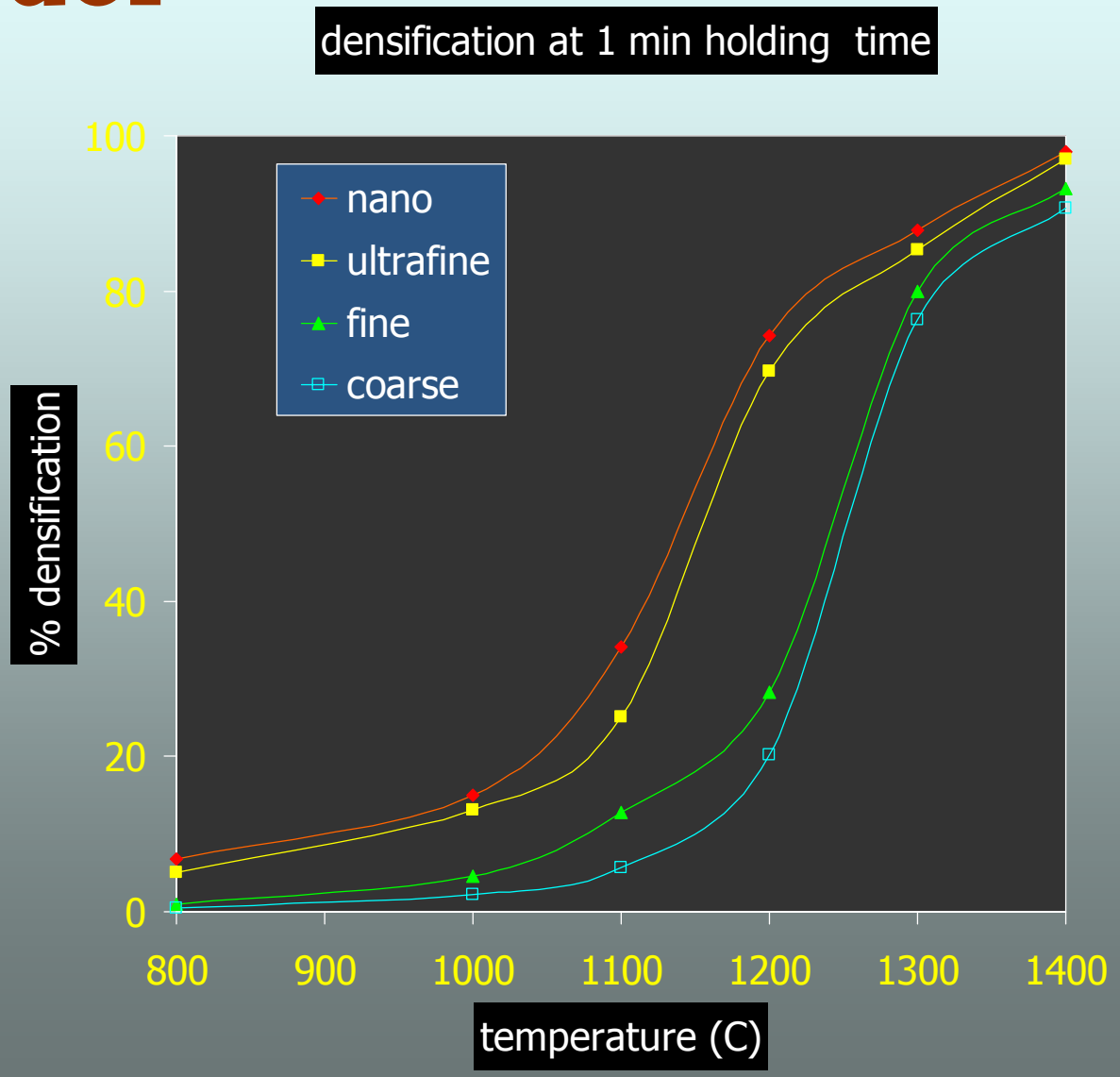
$\Delta H° = -(9.3+21.4x)$ kcal at 1200 K



Sintering of Nanocrystalline WC-Co Powder

State of knowledge on nanostructured WC-Co during sintering

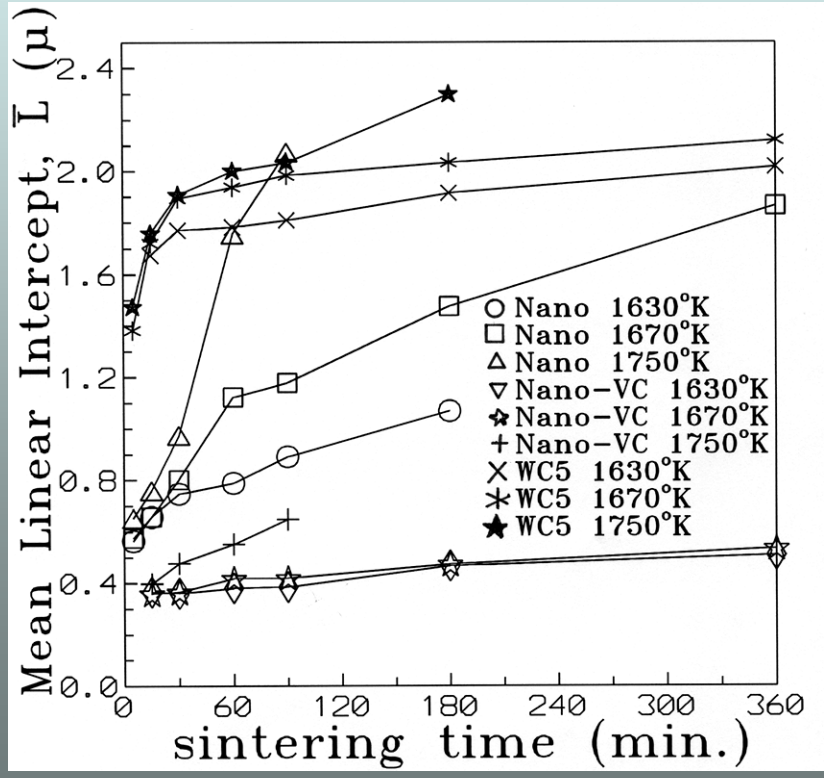
- Interaction between densification and grain growth processes requires contradicting measures
- Grain growth inhibitor is found to reduce the rate of densification
- Significant local grain growth may occur on heating to the isothermal hold



Sintering of Nanocrystalline WC-Co Powder

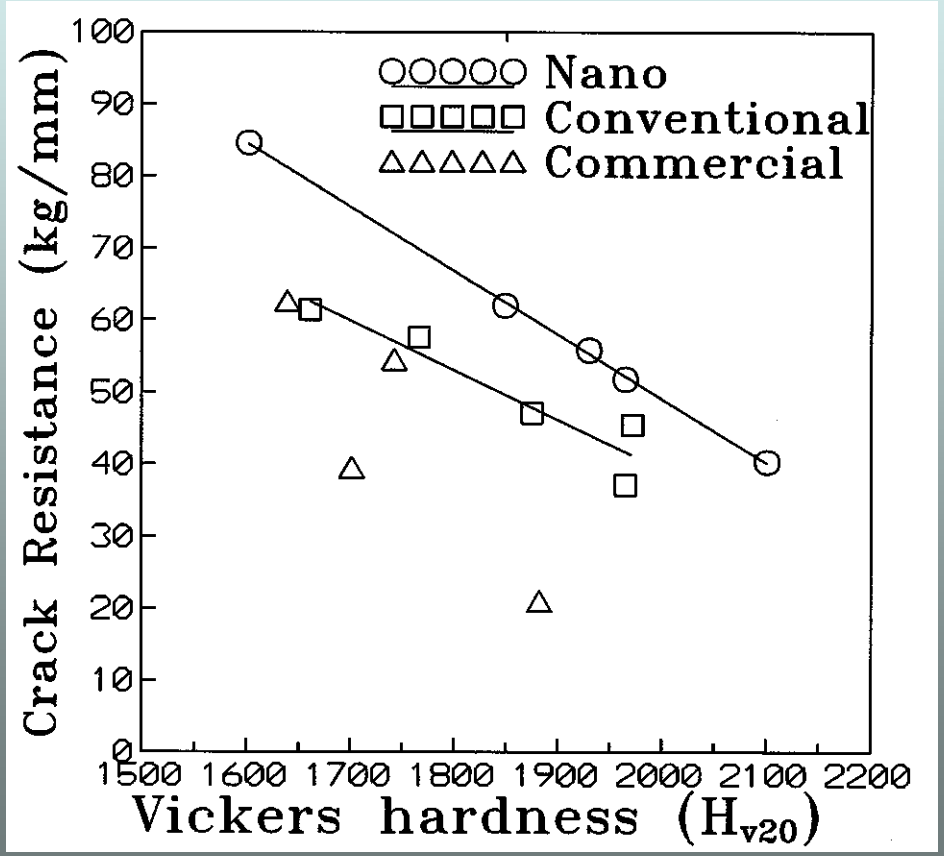
State of knowledge on grain growth of nanostructured WC-Co during sintering

- Grain grows very rapidly in the first five minutes at the temperature during liquid phase sintering
- Solid state sintering by HIPing with a pressure of 1400 MPa produced final grain sizes around 200 to 400 nm
- Grain growth inhibitors are effective for mitigating rapid coarsening of microstructure, but not sufficient for achieving final grain sizes of <100 nm



Nanostructured cemented tungsten carbide - powder processing and ultra-high pressure sintering

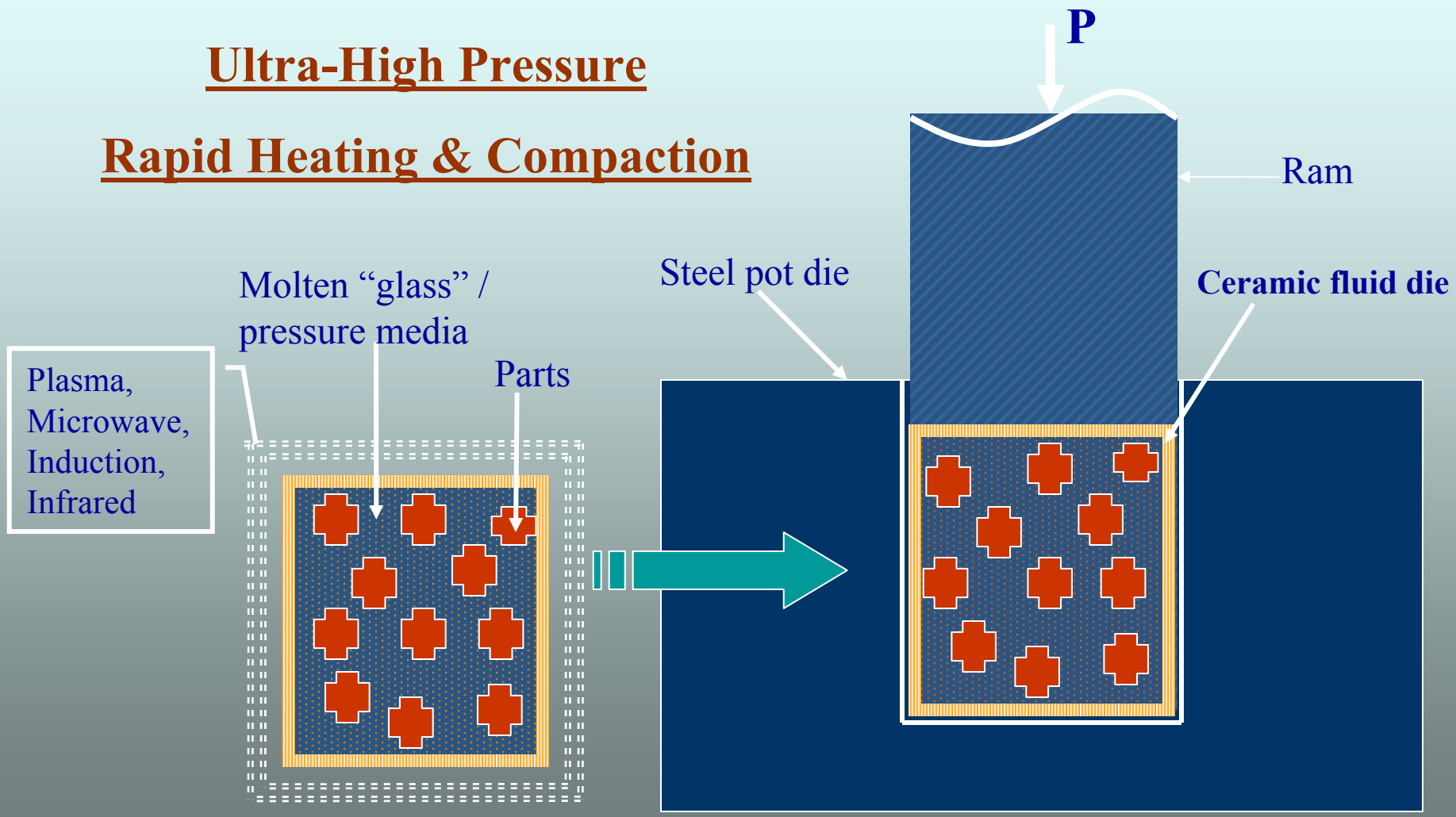
- Previous research has shown unique and promising properties as grain size becomes finer and finer
- Finest sintered grain size so far is between 100 - 200 nm
- LPS, hot pressing, HIPing, solid state, grain growth inhibitors - all tried



nanostructured cemented tungsten carbide - powder processing and ultra-high pressure sintering

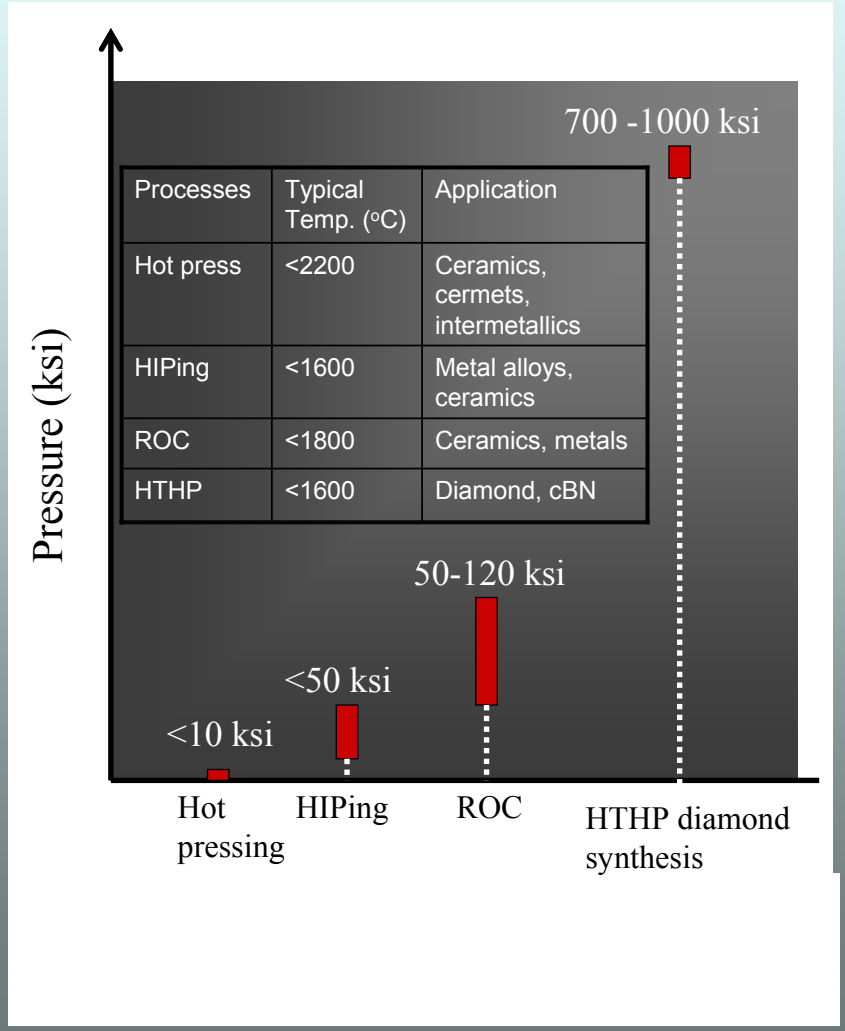
Ultra-High Pressure

Rapid Heating & Compaction



nanostructured cemented tungsten carbide - powder processing and ultra-high pressure sintering

Comparison of Industrial High Pressure Consolidation Technologies



FY 2004 Plan Activities

- Design and build a customized CVS system,
- Identify and study critical processing variables for the synthesis of WC/Co powders via vapor phase reactions
- Study fundamentals of densification and grain growth mechanisms of nanocrystalline WC/Co powder during sintering
- Design and build a rapid heating system
- Design and build a ultrahigh pressure rapid HIPing consolidation system